

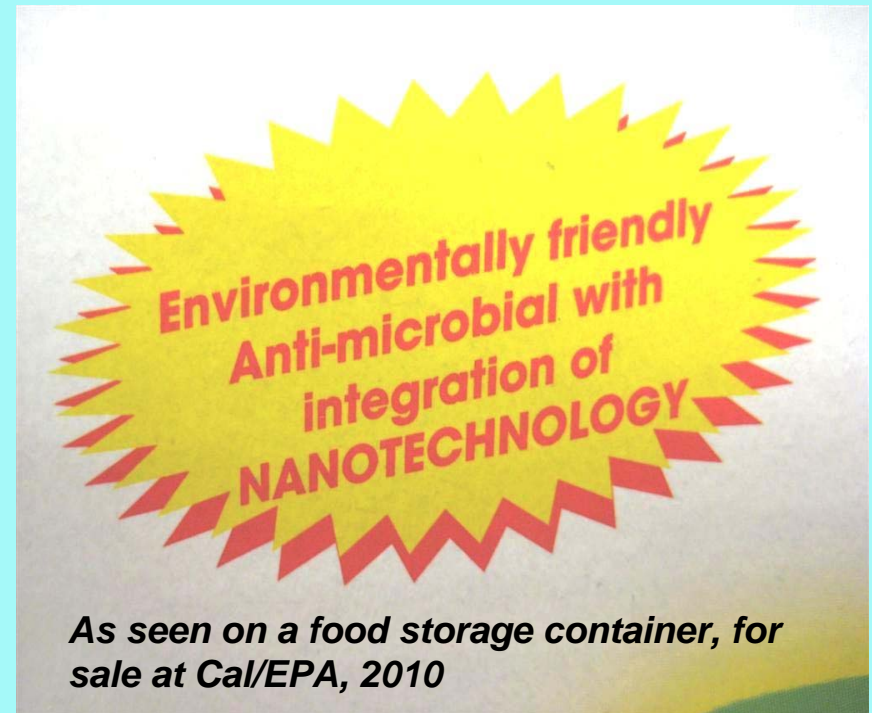
Nanomaterials and AB289 – DTSC's Nano Initiative

DPR's Pesticide Registration and Evaluation Committee

November 9, 2010
Sacramento



“The advent of nanotechnology is considered to be the biggest innovation since the Industrial Revolution”
(Gwinn & Vallyathan, 2006)



National Science Foundation (Roco, 2005) estimates that the worldwide market for nanotechnology products will reach \$1 trillion by 2015.

- A nanoparticle is $\sim 1/80,000$ the diameter of a human hair.
- Nanoparticles are used to create new structures and products that behave differently.
- Nanoparticles exist in nature, but our ability to manipulate them is a new field of study.

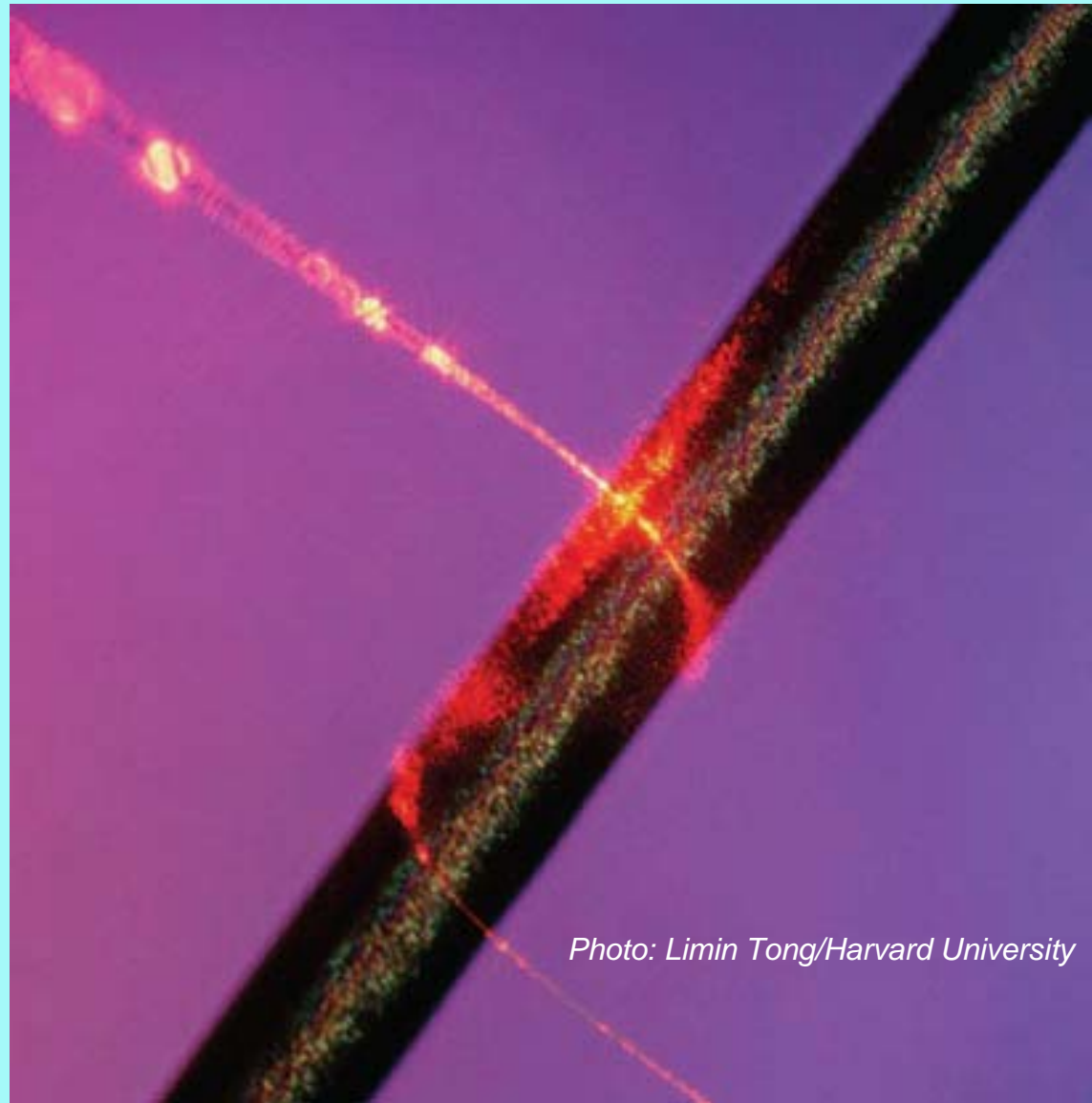


Photo: Limin Tong/Harvard University

A light-conducting silica nanowire wraps a beam of light around strand of human hair. The nanowires are flexible and can be as slender as 50 nanometers in width, about one thousandth the width of a hair.

Nano Products, Publications and Patents Are Increasing Exponentially

Exposure Assessment: Recommendations for Nanotechnology-Based Pesticides

DAVID STONE, BRYAN J. HARPER, ISEULT LYNCH, KENNETH DAWSON,
STACY L. HARPER

- ***Disclosures of nanoparticle characteristics in product formulations;***
- ***Additional uncertainty factors for NBPs with inadequate data;***
- ***Route-specific approaches for assessing exposure;***
- ***Testing with the commercial form of NBPs;***
- ***Initiation of a health surveillance program;***
- ***Development of educational programs.***

International Journal of Occupational and Environmental Health,
Oct/Dec 2010

The single largest category of nano-enabled products are the nanosilvers



Nano Silver Anti-microbial Towel

Made in China. "Through the patented nanotechnology, the towel is impregnated with nano-silver particles. While maintaining the feature of refine cotton, it is non-toxic, non-stimulating and with stronger effect when it is in contact with water. Thus its anti-bacterial and anti-odour functions are enhanced in moisturized environments. It is effective in maintaining personal hygiene. "

Strong Antimicrobial Coatings: Single-Walled Carbon Nanotubes Armored with Biopolymers

*Dhriti Nepal, Shankar Balasubramanian, Aleksandr L. Simonian,
and Virginia A. Davis -*

*Department of Chemical Engineering and Materials Research and Education Center,
Samuel Ginn College of Engineering, Auburn UnVersity, Auburn, Alabama 36849*

Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products

KIM, PARK, MURAYAMA, AND HOCHELLA

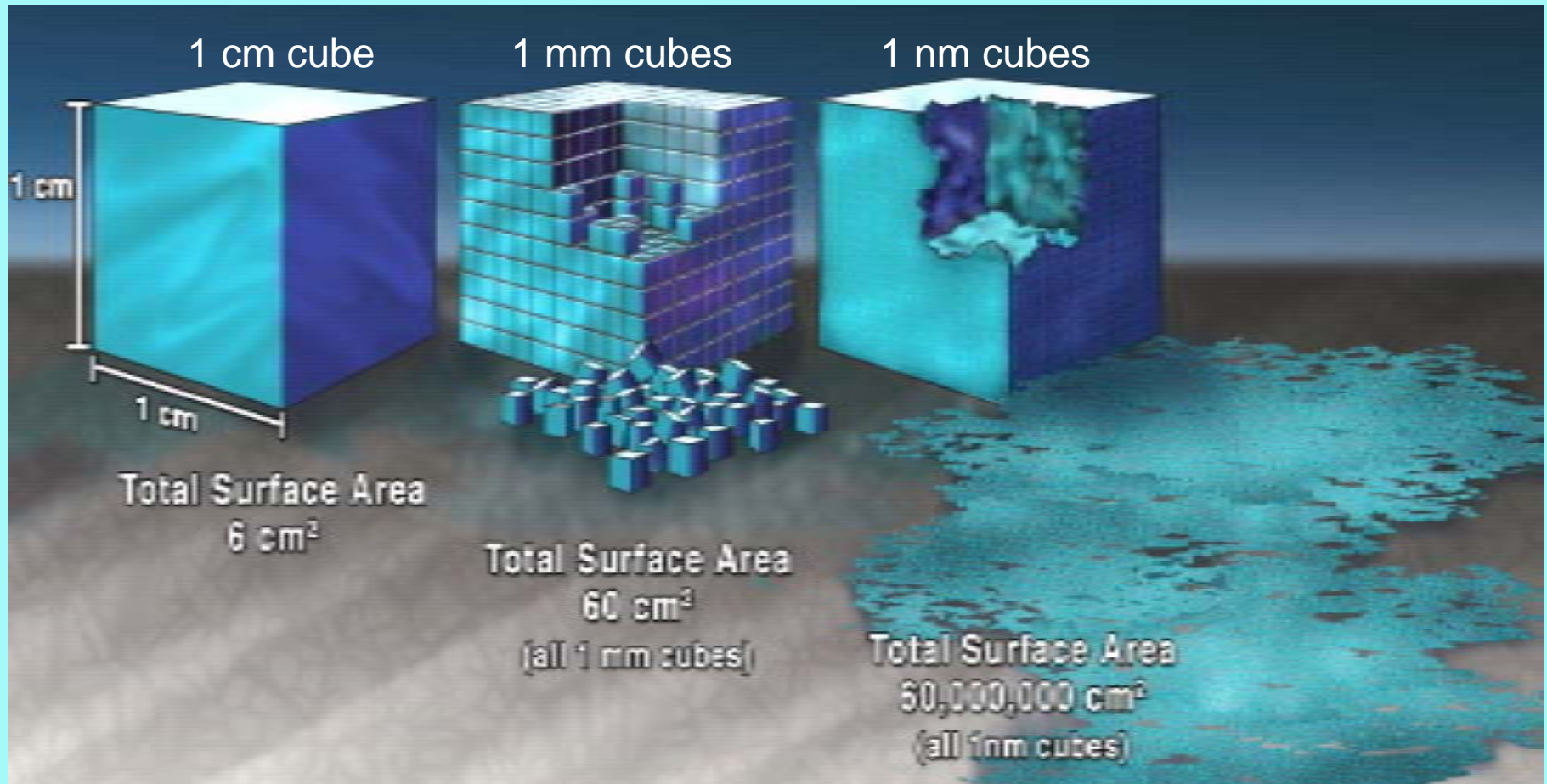
*The Center for NanoBioEarth, Department of Geosciences,
Virginia Tech, Department of Materials Science and Engineering*

“Considering the current extensive production of Ag NPs and their widespread use in consumer products, it is likely that they are entering wastewater streams and the treatment facilities that process this water...”



Why are nanomaterials potentially more dangerous?

Large surface area = more surface molecules



The demand for antimicrobial coatings in the U.S. is expected to grow from \$175M in 2005 to \$550 by 2012.. - *nanowerks*

“Due to the unique antibacterial activity of silver (Ag) (2–5), Ag NPs are one of the most extensively used NPs in consumer products..” -

- Kim, et al, Virginia Tech, ES&T, Sept 2010

Nanosilver Pesticides

EPA addresses data gaps, prepares to register more products

[Britt Erickson](#)



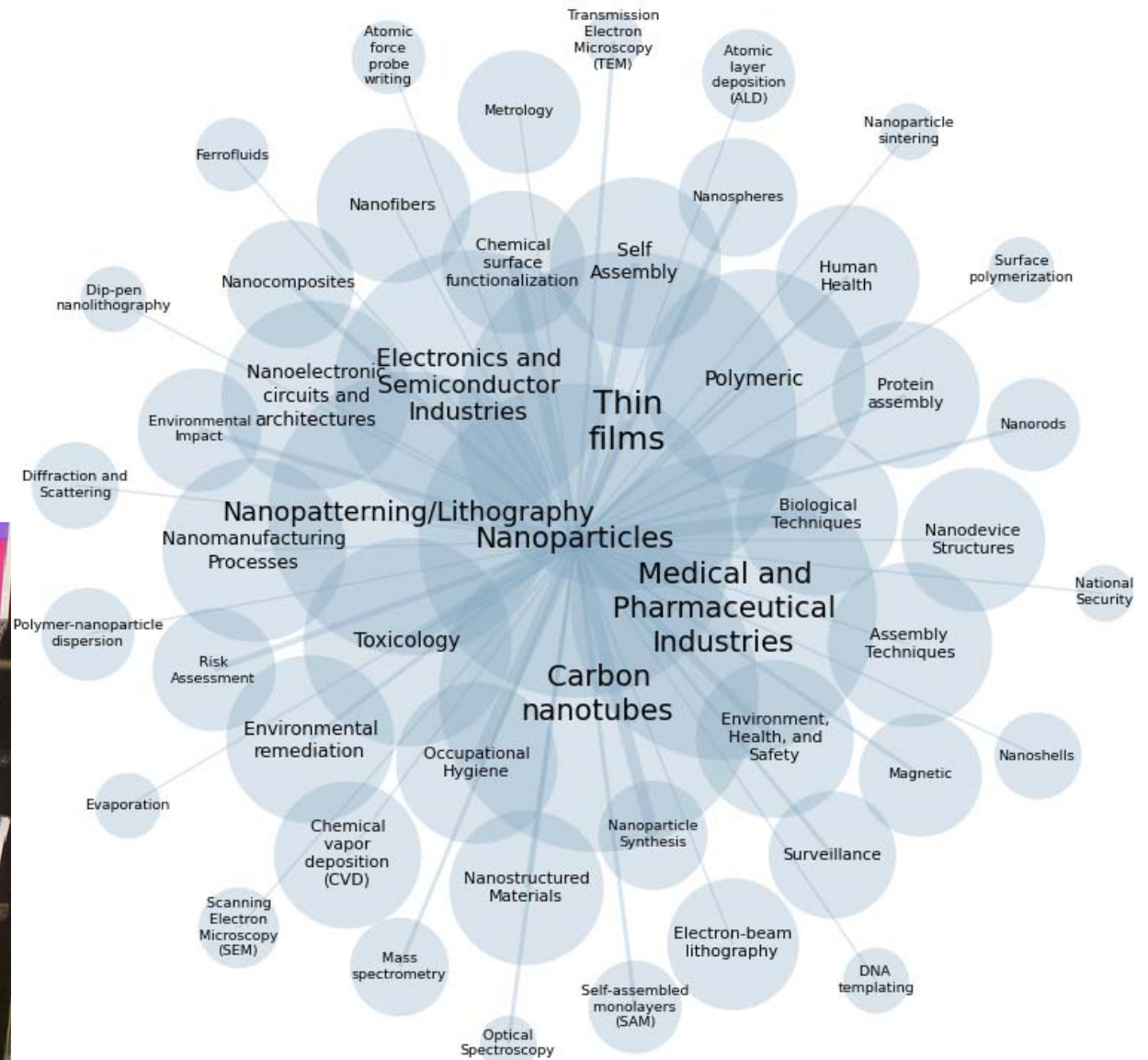
IN THE WASH Studies show a large variation in the amount of silver that leaches from nanosilver textiles during washing.

Chemical and Engineering News – 11/09

Calk and Sealants



(Andrew Maynard/Project on Emerging Nanotechnologies)



Anti-bacti undies

Nanomaterials do differ !

Can't have it both ways.. cannot claim "new properties & performance" and say "it's still the same." *R. Dennison, EDF*

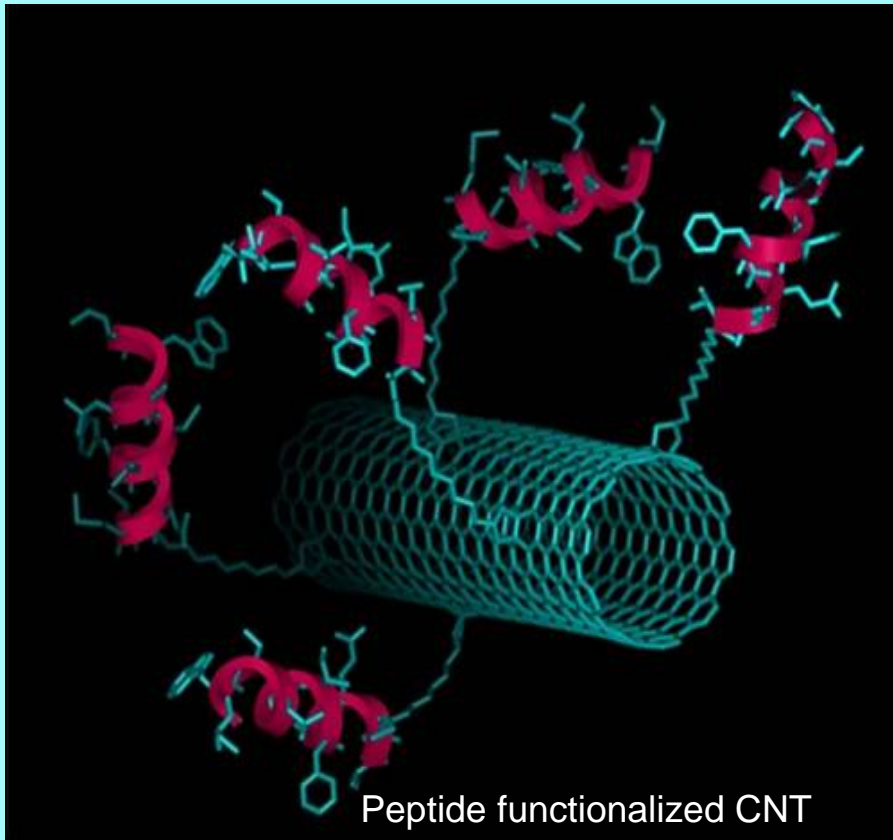
Why are Nanoparticles Different?

Their physical and chemical properties can change with their dimensions.

They are often mixtures, with surfaces that differ from the bulk size counterparts.

They can change in the environment – oxidation, agglomeration, fragmentation, solubility, etc.

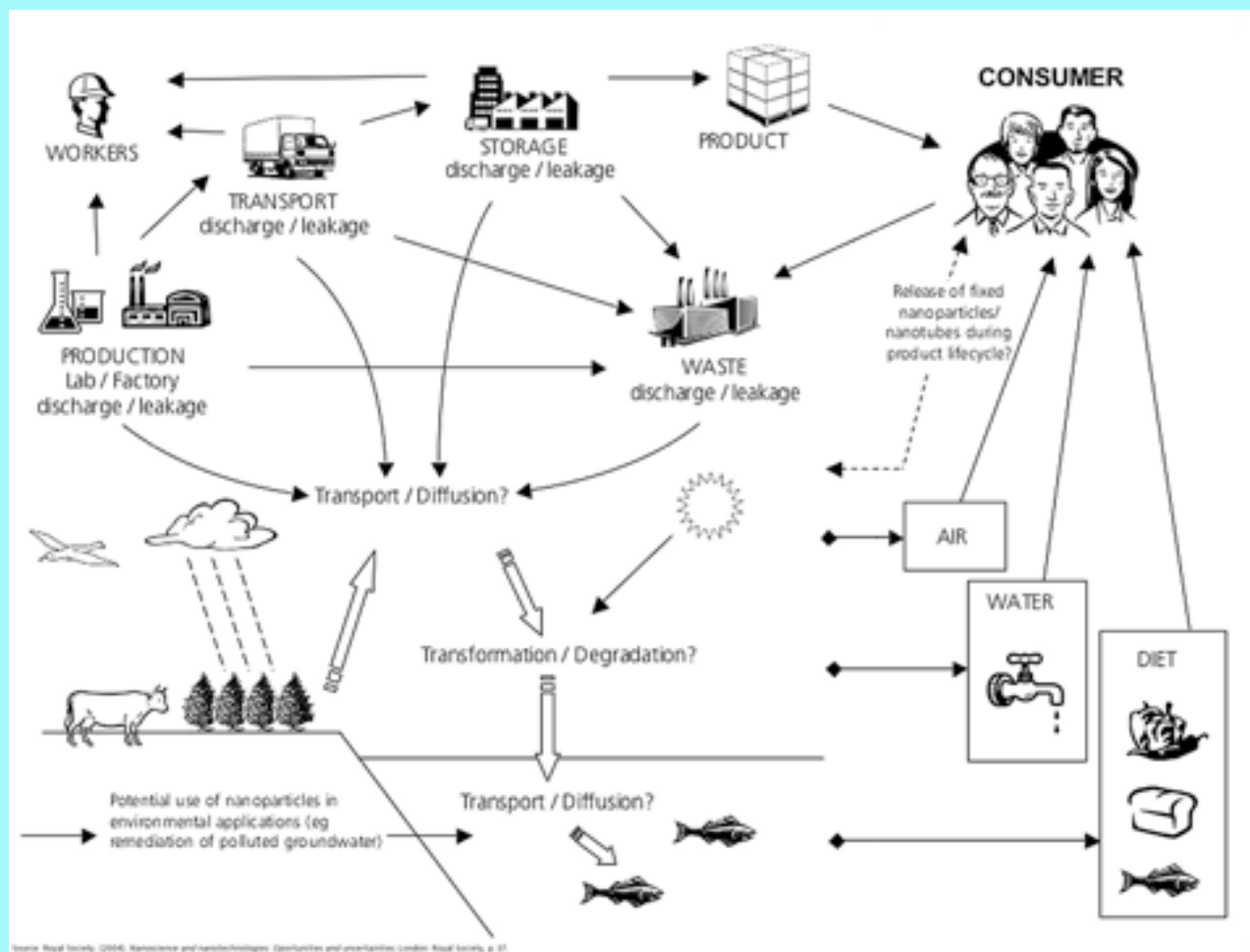
They can be functionalized in novel ways for specific applications



Peptide functionalized CNT

Environmental Points of Entry for Nanomaterials

Exposure Assessment



Analytical Challenges



Hazard ID - Monitoring



- o Conventional wet chemistry analytical approaches are not suitable
- o Optical microscopy is not useful
- o Need for high resolution electron microscopy
 - Atomic Force Microscope
 - Scanning Electron Microscope
 - Transmission Electron Microscopy
 - Scanning Transmission Electron Microscopy
- o Challenges to source identification

California Nanomaterials Initiative at DTSC



Goals -

Get more information into the marketplace.

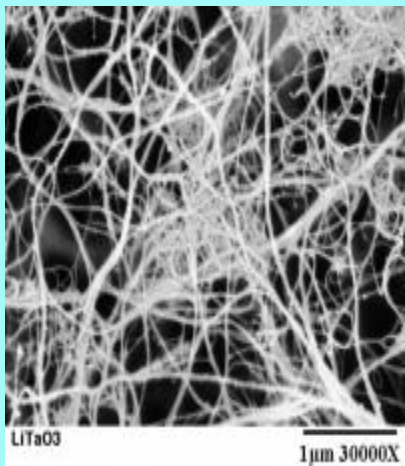
Establish what is known & determine “data gaps.”

Create strategic partnerships with the stakeholders that will fill “data gaps.”

Use strategic partnership with the University of California, Stanford and other academic institutions to fill “data gaps” through the coordinated pursuit of federal support.

Create strategic, coordinated and transparent partnership with the Federal Government.

Create market dominant products through trust.



nanotubes

Data Gaps = Information Needs

For Nano Risk Management



- Physical properties, including:
 - size
 - shape
 - surface area (including biologically available surface area)
 - solubility
 - surface chemistry
 - size distribution
 - Particle and bulk density
 - surface reactivity
 - Porosity
 - Surface charge
- Commercial names
- Common form(s)
- Chemical composition
- Molecular structure
- Crystal structure
- Physical form(s)
- Purity
- Adhesion, diffusion, agglomeration, and aggregation behavior
- Dispersability
- Dose-response and toxicological modes of action
- Routes of exposure into the body
- Octanol-water partition coefficient
- Bioconcentration factor for humans
- Metabolism, including but not limited to bioaccumulation sites
- Analytical test methods, including methods for metabolites and degradation products
- Workplace detection and monitoring
- **Environmental analysis and monitoring**
- Effectiveness of personal protection equipment
- Fate and transport
- Physicochemical properties for characterization to enable prediction for biointeractions
- Stability in liquid and solid matrices, particularly those in commercial use
- Waste handling

AB 289 (2006)

Assembly Member Wilma Chan



Health & Safety Code

Chapter 699, Section 57018 – 57020

it should be the responsibility of those who manufacture or import a chemical to provide relevant information on the fate and transport of that chemical into the environment

"Manufacturer" means a person who produces a chemical in this state or who imports a chemical into this state for sale in this state

"Chemical" has the same meaning as a chemical substance, as defined in Section 2602 of Title 15 of the United States Code

WHAT MAY BE REQUESTED ?



The information that the state agency requests may include, but is NOT limited to, any of the following:

- An analytical test method for that chemical, or for metabolites and degradation products for that chemical that are biologically relevant in the matrix specified by the state agency.
- The octanol-water partition coefficient and bioconcentration factor for humans for that chemical.
- Other relevant information on the fate and transport of that chemical in the environment.

AB289 Process



- Identify California manufacturers and information needs for each chemical;
- Search state, federal and intergovernmental databases;
- Build a bibliographic database of the information gathered;
- Identify information needs for each chemical;
- Consult with external experts on information needs (universities, industry associations and others);
- Consult with manufacturers;
- **Post the information request on the DTSC and Cal/EPA web sites;**
- **MAKE FORMAL REQUEST**
- Collaborate with manufacturers to identify additional information needed;
- Manufacturers have up to one year to provide the requested information;
- Protect trade secret claims;
- Organize information as it is received;
- Evaluate/Request additional information, if necessary;
- Share the information.



Round 1 Call-in Questions on Carbon Nanotubes – 2009-2010

Detection and Measurement: What sampling, detection & measurement methods are you using to monitor the presence of your chemical in the workplace & the environment? Provide a full description of all required sampling, detection, measurement and verification methodologies.

Environmental Fate and Transport: What is your knowledge about the current and projected presence of your chemical in the environment that results from manufacturing, distribution, use, and end-of-life disposal?

Public Health & Environmental Impacts: What is your knowledge about the safety of your chemical in terms of occupational safety, public health and the environment?

Occupational Safety: What methods are you using to protect workers in the research, development and manufacturing environment?

Round Two: Nano Metal Oxides and Quantum Dots

- *Announced interest in April 2009*
- *Conducted search for existing information*
- *Convened today's workshop on*
 - **Nano Silver**
 - **Nano Zero Valent Iron**
 - **Nano Titanium Dioxide**
 - **Nano Zinc Oxide**
 - **Nano Cerium Oxide**
 - **Quantum Dots**
- *Focusing initial questions on analytical test methods for the respective nanomaterial chemical, and its metabolites and breakdown products, in various environmental matrices – air, water, soil*
- *Anticipated formal request: Fall 2010*

DTSC / DPR MOU re: nanosilver

- Signed by the directors in May 2010
- Allows DTSC to review pesticide registration documents
- Identify potential nanosilver mfgs / importers
- Assess uses and impacts
- DTSC agrees to maintain confidentiality
- *Dr. Neena Sahasrabudhe is DTSC contact*

Nano silver – Human Health and Environmental Concerns

- Neurotoxin
- Inhibits DNA synthesis and degrades protein function
- Possible human diseases related to inhalation, ingestion

Nanotechnology Resources

ETC Group

An assortment of publications and other materials on nanotechnology and its impacts on society.

Friends of the Earth--Nanotechnology website

Includes the report *Nanomaterial, Sunscreens, and Cosmetics: Small Ingredients, Big Risks*, and a nano-sunscreen, cosmetic and personal care products inventory. Also, visit the [Friends of the Earth Australia's Nanotechnology Project](#)

The Woodrow Wilson International Center for Scholars Project on Emerging Nanotechnologies

This site includes numerous reports and the only searchable nano-consumer product database.

Hazards Magazine-Special Issue on Nanotechnology

This special issue of the UK publication, *Hazards*, contains an extensive review of safety and health issues related to nanotechnologies.

The Royal Society--Royal Academy of Engineering

Seminal 2004 report outlining the risks of nanotechnology.

Environmental Working Group: Nanomaterial Personal Care Products Listing

National Nanotechnology Initiative

The U.S. government's official nanotechnology coordinating office.

The U.S. Food and Drug Administration

The FDA's nanotechnology policy page.

The Center on Nanotechnology and Society

Interdisciplinary center on the societal implications of nanotechnology with a special emphasis on the human condition

Resources, cont'd

The Foresight Institute

A nonprofit organization dedicated to exploring the emerging science of nanotechnology, its benefits, risks, and policy that affects it.

"Titanium Dioxide (P25) Produces Reactive Oxygen Species in Immortalized Brain Microglia: Implications for Nanoparticle Neurotoxicity"

Study showing manufactured nanoparticles of titanium dioxide - used in many nano-sunscreens and nano-cosmetics - at low concentrations can produce harmful free radicals in brain cells and the potential for brain cell damage.

"Correlation Between Particle Size, In Vitro Particle Persistence, and Lung Injury"

An *Environmental Health Perspectives* article detailing how nanoscale particles cause noticeably more lung inflammation and injury than their microscale equivalents.

"Manufactured Nanomaterials (Fullerenes, C60) Induce Oxidative Stress in the Brain of Juvenile Largemouth Bass"

An *Environmental Health Perspectives* article describing how largemouth bass experienced brain damage when nanosized fullerenes were placed in their habitat.

Nanoparticles: An Occupational Hygiene Review, Institute of Occupational Medicine, Research Report 274

2004 study gives an overview of nanoparticle exposure and examines the routes, sources, levels of exposure, control measures, and exposure numbers.

Swiss Re, Nanotechnology: Small Matter, Many Unknowns

2004 overview study that addresses the risk issues associated with nanotechnology from an insurability perspective.

Nanowerk

Nanowerk- an extensive nanomaterial database; nanorisk newsletter

"Toxic potential of materials at the nanolevel", Nel et al.

2006 article published in *Science* discussing the toxicity and mobility hazards to human health of nanomaterials.

Allianz Group and OECD, Small size that matter: Opportunities and risks of nanotechnologies

2005 joint study